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(54) Title: MODIFIED SOLID OXIDE CATALYST AND PROCESS FOR PRODUCING SAME

(57) Abstract

A catalyst comprises a hydrogenation/dehydrogenation component, such as a noble metal, deposited on an acidic solid product formed by modifying a Group IVB metal oxide with an oxyanion of a Group VIB metal. An example of this catalyst is platinum deposited on zirconia modified with tungstate. The catalyst may be used, for example, to isomerize C_4 to C_8 paraffins.

No Sulfate

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MODIFIED SOLID OXIDE CATALYST AND PROCESS FOR PRODUCING SAME

This invention relates to a modified solid oxide catalyst and a process of producing the catalyst. This catalyst may be used, for example, to isomerize C_4 to C_8 paraffins.

The isomerization of paraffins, especially light paraffins, is an established refining process which is traditionally used to provide additional feedstock for alkylation units or to convert relatively low octane linear paraffins to higher octane, branched chain isomers which can be blended into the gasoline pool. Straight chain paraffins such as n-butane, n-pentane and n-hexane are converted to the corresponding isoparaffins by various isomerization processes which may use various types of catalysts. Non-regenerable Lewis and Bronsted acid catalysts may be used, for example, as disclosed in U.S. Patent Nos. 3,766,286; 3,852,184; 3,855,346; 3,839,489; 4,144,282; and 4,814,544. Commercial processes of this type have been developed by various companies including Phillips Petroleum Company (Catalytic Isomerization) and Shell Development Company (Liquid Phase Isomerization).

An alternative type of catalyst used in a number of commercial isomerization processes comprises a metal hydrogenation/dehydrogenation component, usually platinum, on a porous support. An example of this process is the Penex process (UOP) in which the isomerization is carried out in the presence of hydrogen and a platinum catalyst. The Iso-Kel process (M.W. Kellogg) also employs a precious metal catalyst with hydrogen circulation and the Pentafining (Arco/Englehardt) and Butamer (UOP) processes also employ platinum on supports with external hydrogen circulation. Processes of this kind are disclosed, for example, in U.S. Patent Nos. 4,834,866 (Schmidt) and 4,783,575 (Schmidt).

Isomerization processes utilizing metal components on supports comprising a molecular sieve are disclosed in U.S. Patent Nos. 3,842,114 (Sie); 3,836,597 (Sie); 4,778,944 (Zarchy) and 4,374,296 (Haag).

Paraffin isomerization catalysts may also be employed as ring opening catalysts for the removal of cyclic aromatic precursors from reformer feedstocks as disclosed in U.S. 4,783,575 (Schmidt) and U.S. 4,834,866 (Schmidt). For example, cyclohexane, a precursor of benzene, may be isomerized to a mixture of branched paraffins which are only partly aromatized in the reformer so as to minimize the production of benzene. U.S. Patent No. 3,631,117 describes a process for the hydroisomerization of cyclic hydrocarbons that uses a zeolite supported Group VIII metal as a catalyst for ring opening and paraffin isomerization. The utilization of paraffin isomerization for ring opening aromatic precursors, especially cyclohexane, is likely to become more important in the future as environmental regulations limit the aromatic content, particularly the benzene content, of motor gasoline.

According to one aspect of the invention, there is provided a catalyst comprising (i) an acidic solid product formed by modifying a Group IVB metal oxide with an oxyanion of a Group VIB metal and (ii) an hydrogenation/dehydrogenation component deposited on said solid product.

According to a further aspect of the invention, there is provided a process for preparing the catalyst of said one aspect of the invention comprising the steps of:

(a) contacting the hydroxide or hydrated oxide of a Group IVB metal with an aqueous solution comprising a source of an oxyanion of a Group VIB metal to form an acidic solid product comprising oxygen, Group IVB metal and Group VI metal; and then

(b) depositing a hydrogenation/dehydrogenation component on the solid product of step (a).

According to yet a further aspect of the invention, there is provided a process for isomerizing a C_4 to C_8 paraffin feed comprising contacting the feed with the catalyst according to said one aspect of the invention.

The catalyst described herein comprises an oxide of a Group IVB metal, preferably zirconia or titania. This Group IVB metal oxide is modified with an oxyanion of a Group VIB metal, such as an oxyanion of tungsten, such as tungstate. The modification of the Group IVB metal oxide with the oxyanion of the Group VIB metal imparts acid functionality to the material. The modification of a Group IVB metal oxide, particularly, zirconia, with a Group VIB metal oxyanion, particularly tungstate, is described in U.S. Patent No. 5,113,034; in Japanese Kokai Patent Application No. 1 [1989]-288339; and in an article by K. Arata and M. Hino in Proceedings 9th International Congress on Catalysis, Volume 4, pages 1727-1735 (1988).

In addition, a hydrogenation/dehydrogenation component is combined with the acidic solid product formed by modifying the Group IVB metal oxide with the oxyanion of a Group VIB metal. This hydrogenation/dehydrogenation component imparts the ability of the material to catalyze the addition of hydrogen to or the removal of hydrogen from organic compounds, such as hydrocarbons, optionally substituted with one or more heteroatoms, such as oxygen, nitrogen, metals or sulfur, when the organic compounds are contacted with the modified metal oxide under sufficient hydrogenation or dehydrogenation conditions.

Examples of hydrogenation/dehydrogenation components include the oxide, hydroxide or free metal (i.e., zero valent) forms of Group VIII metals (i.e., Pt, Pd, Ir, Rh, Os, Ru, Ni, Co and Fe), Group IVA metals (i.e., Sn and Pb), Group VB metals (i.e., Sb and Bi) and Group VIIB metals (i.e., Mn, Tc and Re). The catalyst preferably comprises one or more catalytic forms of one or more noble metals (i.e., Pt, Pd, Ir, Rh, Os or Ru). Combinations of

catalytic forms of such noble or non-noble metals, such as combinations of Pt with Sn, may be used. The valence state of the metal of the hydrogenation/dehydrogenation component is preferably in a reduced valance state, e.g., when this component is in the form of an oxide or hydroxide. The reduced valence state of this metal may be attained, in situ, during the course of a reaction, when a reducing agent, such as hydrogen, is included in the feed to the reaction.

For the purposes of the present disclosure, the expression, Group IVB metal oxide modified with an oxyanion of a Group VIB metal, is intended to connote a material comprising, by elemental analysis, a Group IVB metal, a Group VIB metal and oxygen, with more acidity than a simple mixture of separately formed Group IVB metal oxide mixed with a separately formed Group VIB metal oxide or oxyanion. The present Group IVB metal, e.g., zirconium, oxide modified with an oxyanion of a Group VIB metal, e.g., tungsten, is believed to result from an actual chemical interaction between a source of a Group IVB metal oxide and a source of a Group VIB metal oxide or oxyanion.

This chemical interaction is discussed in the aforementioned article by K. Arata and M. Hino in Proceedings 9th International Congress on Catalysis, Volume 4, pages 1727-1735 (1988). In this article, it is suggested that solid superacids are formed when sulfates are reacted with hydroxides or oxides of certain metals, e.g., Zr. These superacids are said to have the structure of a bidentate sulfate ion coordinated to the metal, e.g., Zr. In this article, it is further suggested that a superacid can also be formed when tungstates are reacted with hydroxides or oxides of Zr. The resulting tungstate modified zirconia materials are theorized to have an analogous structure to the aforementioned superacids comprising sulfate and zirconium, wherein tungsten atoms replace sulfur atoms in the bidentate structure.

Although it is believed that the present catalysts may comprise the bidentate structure suggested in the aforementioned article by Arata and Hino, the particular structure of the catalytically active site in the present Group IVB metal oxide modified with an oxyanion of a Group VIB metal has not yet been confirmed, and it is not intended that the present catalyst component should be limited to any particular structure.

Other elements, such as alkali (Group IA) or alkaline earth (Group IIA) compounds may optionally be added to the present catalyst to alter its catalytic properties. The addition of such alkali or alkaline earth compounds to the present catalyst may enhance the catalytic properties of components thereof, e.g., Pt or W, in terms of their ability to function as a hydrogenation/ dehydrogenation component or an acid component.

The Group IVB metal (i.e., Ti, Zr or Hf) and the Group VIB metal (i.e., Cr, Mo or W) species of the present catalyst are not limited to any particular valence state for these species. These species may be present in the catalyst in any possible positive oxidation value for the species. Subjecting the catalyst, e.g., when the catalyst comprises tungsten, to reducing conditions may enhance the overall catalytic ability of the catalyst to catalyze certain reactions, e.g., the isomerization of n-hexane.

Suitable sources of the Group IVB metal oxide, used for preparing the present catalyst, include compounds capable of generating such oxides, such as oxychlorides, chlorides, nitrates, etc., particularly of zirconium or titanium. Alkoxides of such metals may also be used as precursors or sources of the Group IVB metal oxide. Examples of such alkoxides include zirconium n-propoxide and titanium i-propoxide. Preferred sources of a Group IVB metal oxide are zirconium hydroxide, i.e., $Zr(OH)_4$, and hydrated zirconia. The expression, hydrated zirconia, is intended to connote materials comprising zirconium atoms

covalently linked to other zirconium atoms via bridging oxygen atoms, i.e., Zr-O-Zr, further comprising available surface hydroxy groups. These available surface hydroxyl groups are believed to react with the source of an anion of a Group IVB metal, such as tungsten, to form the present acidic catalyst component. As suggested in the aforementioned article by K. Arata and M. Hino in <u>Proceedings 9th International Congress on Catalysis</u>, Volume 4, pages 1727-1735 (1988), precalcination of $Zr(OH)_4$ at a temperature of 100°C to 400°C results in a species which interacts more favorably with tungstate. This precalcination is believed to result in the condensation of ZrOH groups to form a polymeric zirconia species with surface hydroxyl groups. This polymeric species is referred to herein as a form of a hydrated zirconia.

In a preferred embodiment, the hydrated Group IVB metal oxide, such as hydrated zirconia, is subjected to hydrothermal treatment prior to contact with the source of a Group VIB metal oxyanion, such as tungstate. More particularly, the hydrated Group IVB metal oxide is preferably refluxed in an aqueous solution having a pH of 7 or greater. Without wishing to be bound by any theory, it is theorized that the hydrothermal treatment is beneficial because it increases the surface area of the metal oxide. It is also theoretically possible that the hydrothermal treatment alters surface hydroxyl groups on the hydrated zirconia, possibly in a manner which promotes a more desirable interaction with the source of tungstate later used.

The hydrothermal conditions may include a temperature of at least 50°C, e.g., at least 80°C, e.g., at least 100°C. The hydrothermal treatment may take place in a sealed vessel at greater than atmospheric pressure. However, a preferred mode of treatment involves the use of an open vessel under reflux conditions. Agitation of hydrated Group IVB metal oxide in the liquid medium, e.g.,

by the action of refluxing liquid and/or stirring, promotes the effective interaction of the hydrated oxide with the liquid medium. The duration of the contact of the hydrated oxide with the liquid medium may be at least 1 hour, e.g., at least 8 hours. The liquid medium for this treatment may have a pH of about 7 or greater, e.g., 9 or greater. Suitable liquid mediums include water, hydroxide solutions (including hydroxides of NH_4^+, Na^+, K^+, Mg^{2+}, and Ca^{2+}), carbonate and bicarbonate solutions (including carbonates and bicarbonates of NH_4^+, Na^+, K^+, Mg^{2+}, and Ca^{2+}), pyridine and its derivatives, and alkyl/hydroxyl amines.

Suitable sources for the oxyanion of the Group VIB metal, preferably molybdenum or tungsten, include, but are not limited to, ammonium metatungstate or metamolybdate, tungsten or molybdenum chloride, tungsten or molybdenum carbonyl, tungstic or molybdic acid and sodium tungstate or molybdate.

The hydrogenation/dehydrogenation component of the present catalyst may be derived from Group VIII metals, such as platinum, iridium, osmium, palladium, rhodium, ruthenium, nickel, cobalt, iron and mixtures of two or more thereof. These components may optionally be mixed with components derived from Group IVA metals, preferably Sn, and/or components derived from Group VIIB metals, preferably rhenium and manganese. These components may be added to the catalyst by methods known in the art, such as ion exchange, impregnation or physical admixture. For example, salt solutions of these metals may be contacted with the remaining catalyst components under conditions sufficient to combine the respective components. The metal containing salt is preferably water soluble. Examples of such salts include chloroplatinic acid, tetraammineplatinum complexes, platinum chloride, tin sulfate and tin chloride.

The present catalyst may be prepared, for example, by impregnating the hydroxide or oxide, particularly the hydrated oxide, of the Group IVB metal with an aqueous

solution containing an anion of the Group VIB metal, preferably tungstate or molybdate, followed by drying. The resulting solid acidic product is then calcined, preferably in an oxidizing atmosphere, at temperatures from 500°C to 900°C, preferably from 700°C to 850°C, and more preferably from 750°C to 825°C. The calcination time may be up to 48 hours, preferably for 0.5-24 hours, and more preferably for 1.0-10 hours. In a most preferred embodiment, calcination is carried out at about 800°C for 1 to 3 hours. The hydrogenation/dehydrogenation component of the catalyst (e.g., Group VIII metal, Group VIIB metal, etc.) is combined with the solid acidic product after the calcination step by techniques known in the art, such as impregnation, coimpregnation, coprecipitation and physical admixture. The hydrogenation/ dehydrogenation component may also be combined with the remaining catalyst components before or after these remaining components are combined with a binder or matrix material as described hereinafter.

When a source of the hydroxide or hydrated oxide of zirconium is used, calcination, e.g., at temperatures greater than 500°C, of the combination of this material with a source of an oxyanion of tungsten may be needed to induce the theorized chemical reaction which imparts the desired degree of acidity to the overall material. However, when more reactive sources of zirconia are used, it is possible that such high calcination temperatures may not be needed.

In the present catalyst, of the Group IVB oxides, zirconium oxide is preferred; of the Group VIB anions, tungstate is preferred; and of the hydrogenation/dehydrogenation components, platinum and/or platinum-tin are preferred.

Qualitatively speaking, elemental analysis of the present catalyst will reveal the presence of Group IVB metal, Group VIB metal and oxygen. The amount of oxygen

measured in such an analysis will depend on a number of factors, such as the valence state of the Group IVB and Group VIB metals, the form of the hydrogenation/dehydrogenation component, moisture content, etc. Accordingly, in characterizing the composition of the present catalyst, the quantity of oxygen present may not be informative. In functional terms, the amount of Group VIB oxyanion in the present catalyst may be expressed as that amount which increases the acidity of the Group IVB oxide. This amount is referred to herein as an acidity increasing amount. Elemental analysis of the present catalyst may be used to determine the relative amounts of Group IVB metal and Group VIB metal in the catalyst. From these amounts, mole ratios in the form of XO_2/YO_3 may be calculated, where X is said Group IVB metal, assumed to be in the form XO_2, and Y is said Group VIB metal, assumed to be in the form of YO_3. It will be appreciated, however, that these forms of oxides, i.e., XO_2 and YO_3, may not actually exist, and are referred to herein simply for the purposes of calculating relative quantities of X and Y in the present catalyst. The present catalysts may have calculated mole ratios, expressed in the form of XO_2/YO_3, where X is at least one Group IVB metal (i.e., Ti, Zr, and Hf) and Y is at least one Group VIB metal (i.e., Cr, Mo, or W), of up to 1000, e.g., up to 300, e.g., from 2 to 100, e.g., from 4 to 30.

The amount of hydrogenation/dehydrogenation component present in the catalyst conveniently comprises from 0.001 to 5 wt%, preferably from 0.1 to 2 wt %, of the catalyst, especially when this component is a noble metal.

The catalyst described herein may be used as a catalyst for isomerizing C_4 to C_8 paraffins and preferably for isomerizing n-hexane to 2,2-dimethylbutane. Suitable feeds contain substantial amounts of normal and/or singly branched low octane C_4 to C_8 hydrocarbons. The feed may also contain appreciable amounts of C_6 and C_7 cyclic paraffins which may undergo ring-opening reactions.

The present isomerization process may be carried out by contacting the hydrocarbon feed in either liquid or gas phase with the solid catalyst at temperatures less than 500°C, preferably 90 to 425°C, and more preferably 150 to 370°C, and at pressure of 100 to 20,000 kPa (1 to 200 atmospheres), preferably 100 to 10,000 kPa (1 to 100 atmospheres), more preferably 500 to 5,000 kPa (5 to 50 atmospheres). The isomerization process may be carried out either in the presence or absence of hydrogen, more preferably in the presence of hydrogen. The mole ratio of hydrogen to hydrocarbon is typically in the range of 0.01:1 to 10:1, preferably 0.5:1 to 2:1.

It may be desirable to incorporate the present catalyst with another material to improve its properties. Such materials include active and inactive materials and synthetic or naturally occurring zeolites as well as inorganic materials such as clays, silica, and/or metal oxides. In particular, the catalyst may be composited with a matrix material to form the finished form of the catalyst and for this purpose conventional matrix materials such as alumina, silica-alumina and silica are suitable with preference given to silica as a non-acidic binder. Other binder materials may be used, for example, titania, zirconia and other metal oxides or clays. The active catalyst may be composited with the matrix in amounts from 80:20 to 20:80 by weight, e.g., from 80:20 to 50:50 active catalyst:matrix. Compositing may be done by conventional means including mulling the materials together followed by extrusion of pelletizing into the desired finished catalyst particles.

The catalyst may be treated by conventional pre-sulfiding treatments, e.g., by heating in the presence of hydrogen sulfide, to convert oxide forms of the metal components to their corresponding sulfides.

In the present isomerization process, n-paraffinic and mono-methyl branched paraffinic components are isomerized

to higher branched paraffins which are generally better octane boosters. By way of illustration, the significance of these reactions can be gleaned from a review of the following table of Octane Numbers of Pure Hydrocarbons from P.H. Emmett, ed., Catalysis, Vol. VI (1958).

Octane Numbers of Pure Hydrocarbons

Hydrocarbon	Blending Research Octane Number (clear)
Paraffins:	
n-heptane	0
2-methylhexane	41
3-methylhexane	56
2,2-dimethylpentane	89
2,3-dimethylpentane	87
2,2,3-trimethylbutane	113

The feedstock for the present process may be one which contains significant amounts of C_5+ normal and/or slightly branched paraffins. In addition, the feedstock may contain monocyclic aromatic compounds and/or cyclic paraffins, such as cyclohexane. Among the hydrocarbons having 6 or less carbon atoms in the feedstock, at least 1 wt.%, e.g., at least 5 wt.%, e.g., at least 10 wt.%, e.g., at least 20 wt.%, e.g., at least 30 wt.%, of these hydrocarbons may be cyclic hydrocarbons, e.g., aromatics or cyclic paraffins.

The present catalyst may be used to isomerize C_4-C_8 paraffin hydrocarbons, either as pure compounds or mixtures. In refinery operations, the paraffins will normally be present in mixtures and, in addition to the C_4-C_8 materials, may contain hydrocarbons boiling outside this range; cycloparaffins and aromatics may also be present. Thus, the feed will comprise C_4-C_8 paraffins such as butane, pentane, hexane and these may be present in refinery streams such as raffinate cuts from solvent extraction units, reformer feedstock or pyrolysis gasoline from ethylene crackers. The feeds may also contain cyclic hydrocarbons, e.g., in the form of C_6+ naphthas; the cyclic

materials in such feeds may undergo ring opening reactions in the presence of the catalyst with its associated metal component, to form paraffins which then undergo isomerization to iso-paraffins which can be separated from the cyclics by fractionation with the cyclics being recycled to extinction. In addition to pure paraffin feeds (C_4-C_8), mixed paraffin-olefin feeds containing significant levels of olefin may be utilized.

Higher isomerization activity may be provided by the inclusion of an additional material having Lewis or Brønsted acid activity in the catalyst, especially when the catalyst comprises a porous binder material. For this purpose, both liquid and solid acid materials may be used. Examples of suitable additional acidic materials include aluminum trichloride, boron trifluoride and complexes of boron trifluoride, for example, with water, lower alcohols or esters. The maximum amount which may be added is set by the ability of the support material, especially the binder material, to sorb the added component and is readily determined by experiment.

The present catalyst may be used as the exclusive isomerization catalyst in single or multiple catalyst beds or it may be used in combination with other isomerization catalysts. For example, a feed may be first contacted with a catalyst bed comprising the present catalyst followed by contact with a second catalyst bed comprising a different catalyst, such as Pt on mordenite, Pt on zeolite beta or a chlorided platinum-alumina catalyst, as described in U.S. Patent Nos. 4,783,575 and 4,834,866. The temperature of the first catalyst bed may be higher than the temperature of the second catalyst bed. When the present catalyst is called upon to cause extensive ring opening, especially in an initial catalyst bed, relatively high temperatures, e.g., as high as 500°C, and/or relatively high pressures, e.g., as high as 20,000 kPa (200 atmospheres), may be employed.

Although the use of the present catalyst in isomerization reactions has been emphasized hereinabove, it will be appreciated that this catalyst is useful for a variety of organic, e.g., hydrocarbon, compound conversion processes, especially those requiring the use of a dual-functional (1) acidic and (2) hydrogenation/dehydrogenation catalyst. Such conversion processes include, as non-limiting examples, hydrocracking hydrocarbons with reaction conditions including a temperature of 100°C to 700°C, a pressure of 10 to 3,000 kPa (0.1 to 30 atmospheres), a weight hourly space velocity of 0.1 to 20, and a hydrogen/hydrocarbon mole ratio of 0 to 20; dehydrogenating hydrocarbon compounds with reaction conditions including a temperature of 300°C to 700°C, a pressure of 10 to 1,000 kPa (0.1 to 10 atmospheres) and a weight hourly space velocity of 0.1 to 20; converting paraffins to aromatics with reaction conditions including a temperature of 100°C to 700°C, a pressure of 10 to 6,000 kPa (0.1 to 60 atmospheres), a weight hourly space velocity of 0.5 to 400 and a hydrogen/hydrocarbon mole ratio of 0 to 20; converting olefins to aromatics, e.g., benzene, toluene and xylenes, with reaction conditions including a temperature of 100°C to 700°C, a pressure of 10 to 6,000 kPa (0.1 to 60 atmospheres), a weight hourly space velocity of 0.5 to 400 and a hydrogen/hydrocarbon mole ratio of 0 to 20; transalkylating aromatic hydrocarbons in the presence of polyalkylaromatic hydrocarbons with reaction conditions including a temperature of 200°C to 500°C, a pressure of 100 to 20,000 kPa (1 to 200 atmospheres), a weight hourly space velocity of 10 to 1000 and an aromatic hydrocarbon/polyalkylaromatic hydrocarbon mole ratio of 0.3/1 to 20/1, and a hydrogen/hydrocarbon mole ratio of 0 to 20; and transferring hydrogen from paraffins to olefins with reaction conditions including a temperature of -25°C to 400°C, e.g., 75°C to 200°C, a pressure from below 100 kPa to 34,500 kPa (below atmospheric to 5000 psig, e.g.,

from 100 to 7,000 kPa (1 to 1000 psig, a mole ratio of total paraffin to total olefin of 1:2 to 500:1, e.g., 5:1 to 100:1; and a weight hourly space velocity based on olefin of 0.01 to 100, e.g., 0.05 to 5.

The present catalyst may also be used in various hydroprocessing reactions, such as the removal of metals, nitrogen and/or sulfur from feedstocks, such as resids, including such elements, particularly in the form of heteroatoms. These hydroprocessing reactions comprise contacting the feedstock along with a sufficient amount of hydrogen with the present catalyst under conditions sufficient to remove metals, nitrogen, and/or sulfur.

Example 1

This Example describes the preparation of a tungstate modified zirconia catalyst. One part by weight of zirconyl chloride, $ZrOCl_2 \cdot 8H_2O$, was added to 3 parts by weight of a 10 M NH_4OH solution. The resulting slurry, $Zr(OH)_4$, was filtered and washed with 5 parts of distilled deionized water, then air dried at 140°C for 8 hours. Approximately 7.5 parts by weight of the resulting $Zr(OH)_4$ were impregnated via incipient wetness with 2.2 parts of an aqueous solution containing 1 part of ammonium metatungstate, $(NH_4)_6H_6W_{12}O_{40}$. The resulting material was dried for 2 hours at 120°C and then calcined at 800°C in flowing air for 2 hours. The sample was calcined at 500°C for 1 hour under flowing nitrogen prior to catalytic testing. This sample had a calculated mole ratio of ZrO_2/WO_3 of 11.6.

Example 2

A platinum and tungstate modified zirconia catalyst was prepared by incipient wetness co-impregnation of H_2PtCl_6 and $(NH_4)_6H_6W_{12}O_{40}$ onto $Zr(OH)_4$. More particularly, to 181.8 parts by weight of $Zr(OH)_4$ were added, via incipient wetness impregnation, 54.5 parts of an aqueous solution containing 24.4 parts of $(NH_4)_6H_6W_{12}O_{40}$ and 1 part of H_2PtCl_6. The resulting material was then dried for 2 hours at 120°C,

and then air calcined at 800°C for 2 hours. This platinum-containing catalyst was calcined at 500°C for 1 hour in flowing nitrogen and then reduced with flowing hydrogen at 300°C for approximately 2 hours prior to catalytic testing. This catalyst had a calculated mole ratio of ZrO_2/WO_3 of 11.6 and contained 100 ppm of Pt based on the total weight of the catalyst.

Example 3

A catalyst was prepared in the same manner as in Example 2 except that more H_2PtCl_6 was used in the co-impregnation step. This catalyst had a calculated mole ratio of ZrO_2/WO_3 of 11.6 and contained 0.2 wt.% of Pt based on the total weight of the catalyst.

Example 4

A catalyst was prepared in the same manner as in Example 2 except that more H_2PtCl_6 was used in the co-impregnation step.
This catalyst had a calculated mole ratio of ZrO_2/WO_3 of 11.6 and contained 2 wt.% of Pt based on the total weight of the catalyst.

Examples 5-8

The catalysts of Examples 1-4 were tested in the isomerization of n-hexane. The n-hexane isomerization reactions were carried out in a fixed-bed down-flow reactor. Liquid n-hexane was fed into the reactor using a high pressure pump. Hydrogen was charged through a mass flow controller. Products were analyzed by gas chromatography. The experiments were performed at 260°C, LHSV = 1.8 cc n-C_6 per cc catalyst per hour, 3,200 kPa (450 psig), and a H_2/n-C_6 mol ratio of 1.4.

The experimental results shown in Table 1 indicate that the addition of small amounts of platinum to the catalyst greatly improves the n-hexane isomerization activity to yield the desirable high-octane dimethyl butanes.

In the Tables which follow, the following

abbreviations will be understood: n-C_6 (n-hexane); 3-MP (3-methylpentane); 2-MP (2-methylpentane); 2,3-DMB (2,3-dimethylbutane); 2,2-DMB (2,2-dimethylbutane); i-C_5 (isopentane); n-C_5 (n-pentane); C_4- (hydrocarbons having 4 or less carbon atoms); C_7+ (hydrocarbons having 7 or more carbon atoms); CH (cyclohexane); MCP (methylcyclopentane); BZ (benzene); C_3- (hydrocarbons having 3 or less carbon atoms); i-C_4 (isobutane); n-C_4 (n-butane); and C_5+ (hydrocarbons having 5 or more carbon atoms).

Table 1

Example	Catalyst	Conv. (wt.%)	n-C_6	3-MP	2-MP	2,3-DMB	2,2-DMB	i-C_5	n-C_5	C_4-	Other*
5	Example 1	67.1	32.9	19.1	28.9	7.8	3.7	2.9	0.6	2.0	2.0
6	Example 2	73.2	26.8	21.3	32.2	8.8	4.7	2.5	0.5	1.2	2.0
7	Example 3	79.9	20.1	20.3	30.0	8.0	9.3	4.9	1.6	3.4	2.2
8	Example 4	84.3	15.7	18.7	29.1	8.5	15.5	5.4	1.7	2.3	3.2

* Other is C_7+, cyclohexane (CH), and methylcyclopentane (MCP)

Examples 9 and 10

The catalyst of Example 3 (0.2 wt.% Pt and a calculated mole ratio of ZrO_2/WO_3 of 11.6) was tested at lower temperature, 220°C, and lower LHSV. The results are presented in Table 2 and indicate that high yields of isomerate are obtained.

Table 2

Example	LHSV (hr^{-1})	Conv. (wt.%)	n-C_6	3-MP	2-MP	2,3-DMB	2,2-DMB	i-C_5	n-C_5	C_4-	Other*
9	0.4	86.4	13.6	16.8	26.5	7.8	16.7	8.0	2.8	4.8	2.9
10	0.6	83.1	16.9	20.1	31.8	9.3	11.7	3.7	0.7	2.5	3.2

[1]* Other is C_7+, cyclohexane (CH), and methylcyclopentane (MCP)

Example 11

In this Example platinum was added to the tungstate modified zirconia material after the 800°C air calcination step. 72.5 parts by weight of $Zr(OH)_4$, preparation given in Example 1, were impregnated with 21.7 parts of an aqueous solution containing 12.2 parts of $(NH_4)_6H_6W_{12}O_{40}$. The resulting material was dried for 2 hours at 120°C and then calcined in air at 800°C for 2 hours. After cooling to room temperature, a second incipient wetness impregnation was performed; this time, 1 part of H_2PtCl_6 dissolved in 21.7 parts of distilled water were added. The catalyst was dried at 120°C for 2 hours, calcined in flowing air at 350°C for 3 hours, and then reduced with hydrogen at 300°C for approximately 2 hours. This catalyst contained 0.5 wt.% of Pt based on the total weight of the catalyst.

Example 12

The platinum and tungstate modified catalyst of Example 11 was tested for n-hexane isomerization at 260°C, 3,200 kPa (450 psig), LHSV = 0.6 hr^{-1}, and a $H_2/n\text{-}C_6$ mole ratio of 1.4. Results are given in Table 3.

Table 3

Example	Catalyst	Conv. (wt.%)	n-C_6	3-MP	2-MP	2,3-DMB	2,2-DMB	i-C_5	n-C_5	C_4-	Other*
12	Example 11	83.4	16.6	19.6	29.9	8.3	17.5	3.4	1.5	2.9	traces

* Other is C_7+, cyclohexane (CH), and methylcyclopentane (MCP)

Example 13

Zirconium hydroxide, $Zr(OH)_4$ was synthesized by rapidly hydrolyzing $Zr(O)Cl_2$ in a 10 M NH_4OH solution. The slurry was then pulverized for 30 minutes, filtered, washed with DI water, vacuum dried for 4 hours, and dried at 140°C for 8 hours.

Tungstate modified zirconia was prepared by impregnating $Zr(OH)_4$ with ammonium metatungstate, $(NH_4)_6H_6W_{12}O_{40}$. Drying of the resultant sample was performed for 2 hours at 120°C and then calcined at 800°C. The material was cooled down to ambient temperature before Pt was added via incipient wetness using H_2PtCl_6. The platinum-containing catalyst was calcined at 400°C for 2 hours in flowing air, and then reduced with flowing hydrogen at 300°C for approximately 2 hours. The catalyst had a calculated mole ratio of ZrO_2/WO_3 of 11.6 and contained 0.5 wt.% Pt based on the total weight of the catalyst.

Examples 14 and 15

These Examples illustrate the results obtained on simultaneous ring opening of C_6 cyclic hydrocarbons and n-hexane isomerization over the catalyst of Example 13. A synthetic feedstock having the composition given in Table 4 was used in these experiments. The product composition and operating conditions are presented in Table 5. Results indicate that the catalyst of this invention exhibits high activity for ring opening, while maintaining high C_5+ yield and high paraffin isomerization selectivity to more highly branched paraffins.

Table 4

FEED COMPOSITION

Component	Wt.%
n-Hexane (n-C_6)	50.0
Methylcyclopentane (MCP)	14.5
Cyclohexane (CH)	31.7
Benzene (BZ)	3.9

Table 5

Example	2	3
Reaction Conditions		
Reactor temperature (°C)	260	288
Reactor pressure (psig)	450	450
(kPa)	3,200	3,200
LHSV (hr^{-1})	0.54	0.54
H_2/C_6-mixture (mol/mol)	2	2
Product Composition (wt.%)		
C_3-	tr	0.7
i-C_4	1.3	5.3
n-C_4	0.4	2.0
i-C_5	2.4	7.5
n-C_5	0.9	3.7
2,2-DMB	9.3	11.4
2,3-DMB	6.1	6.2
2-MP	22.3	22.8
3-MP	14.7	15.3
n-C_6	12.6	13.5
MCP	20.4	8.4
CH	6.3	2.0
BZ	0	0
C_7+	3.3	1.1
C_5+ Yield (wt.%)	98.3	92.0
Reactant Conversion (%)		
Ring Opening	46.6	79.2
n-C_6	74.8	73.0

Example 16

This Example describes the preparation of a hydrous ZrO_2 support. One part by weight of zirconyl chloride, $ZrOCl_2 \cdot 8H_2O$, was dissolved in 10 parts H_2O and concentrated $NH_4OH_{(aq)}$ added until the solution pH was ~9. The resulting slurry, $Zr(OH)_4$, was filtered and washed with 10 parts of distilled, deionized water. The solid was air dried at 130°C for 16 hours.

Example 17

This Example describes the preparation of a WO_x/ZrO_2 catalyst from the zirconia support described in Example 16. Approximately 5.6 parts by weight of the dried product from Example 16 was impregnated via incipient wetness with 4.2 parts of an aqueous solution containing 1 part of ammonium metatungstate, $(NH_4)_6H_6W_{12}O_{40}$. The resulting material was dried in air and then calcined at 825°C in air for 3 hours.

Example 18

This Example describes the preparation and use of a $Pt/WO_x/ZrO_2$ catalyst from the resultant product described in Example 17. To 1 part of an 8% H_2PtCl_6 solution was added 2.5 parts of H_2O. This mixture was then used to impregnate by incipient wetness 7 parts of the dried product (at 130°C) from Example 17. The catalyst was then calcined at 300°C in air for 2 hours. This catalyst was designated Catalyst A. In the catalytic experiments, Catalyst A was reduced with H_2 (100 cc/min) at 300°C and atmospheric pressure for 4 hours. The unit was then brought to the desired conditions and hexane feed introduced. Catalytic data and results are given in Table 6.

Example 19

This Example describes the preparation of another WO_x/ZrO_2 catalyst using the zirconia support described in Example 16. Approximately 2.4 parts by weight of the dried product from Example 16 was impregnated via incipient wetness with 2.6 parts of an aqueous solution containing 1

part of ammonium metatungstate. The resulting material was dried in air and then calcined at 825°C in air for 3 hours.

Example 20

This Example describes the preparation and use of a $Pt/WO_x/ZrO_2$ catalyst from the resultant product described in Example 19. To 1 part of an 8% H_2PtCl_6 solution was added 2.5 parts of H_2O. This mixture was then used to impregnate by incipient wetness 7 parts of the dried product (at 130°C) from Example 19. The catalyst was then calcined at 300°C in air for 2 hours. This catalyst was designated Catalyst B. In the catalytic experiments, Catalyst B was reduced with H_2 (100 cc/min) at 300° and atmospheric pressure for 18 hours. The unit was then brought to the desired conditions and hexane feed introduced. Catalytic data and results are given in Table 7.

Example 21

This Example describes the preparation of a hydrothermally treated zirconia support. One part by weight of the filtered wet cake from Example 16 was mixed with 10 parts of distilled, deionized water and the pH of the mixture set to pH ~9 with concentrated $NH_4OH_{(aq)}$. This mixture was refluxed for 16 hours, cooled, filtered, and washed with 10 parts of water. The solid was air dried at 130°C for 16 hours.

Example 22

This Example describes the preparation of a WO_x/ZrO_2 catalyst from the zirconia support described in Example 21. Approximately 5.6 parts by weight of the dried product from Example 21 was impregnated via incipient wetness with 4.2 parts of an aqueous solution containing 1 part of ammonium metatungstate. The resulting material was dried in air and then calcined at 825°C in air for 3 hours.

Example 23

This Example describes the preparation and use of a $Pt/WO_x/ZrO_2$ catalyst from the resultant product in Example 22. To 1 part of an 8% H_2PtCl_6 solution was added 2.5 parts

of H_2O. This mixture was then used to impregnate by incipient wetness 7 parts of the dried product (at 130°C) from Example 22. The catalyst was then calcined at 300°C in air for 2 hours. This catalyst was designated Catalyst C. In the catalytic experiments, Catalyst C was reduced with H_2 (100 cc/min) at 300°C and atmospheric pressure for 4 hours. The unit was then brought to the desired conditions and hexane feed introduced. Catalytic data and results are given in Table 8.

Example 24

This Example describes the preparation of another WO_x/ZrO_2 catalyst using the zirconia support described in Example 21. Approximately 3.4 parts by weight of the dried product from Example 21 was impregnated via incipient wetness with 2.6 parts of an aqueous solution containing 1 part of ammonium metatungstate. The resulting material was dried in air and then calcined at 825°C in air for 3 hours.

Example 25

This Example describes the preparation and use of a $Pt/WO_x/ZrO_2$ catalyst from the resultant product described in Example 24. To 1 part of an 8% H_2PtCl_6 solution was added 2.5 parts of H_2O. This mixture was then used to impregnate by incipient wetness 7 parts of the dried product (at 130°C) from Example 24. The catalyst was then calcined at 300°C in air for 2 hours. This catalyst was designated Catalyst D. In the catalytic experiments, Catalyst D was reduced with H_2 (100 cc/min) at 300°C and atmospheric pressure for 18 hours. The unit was then brought to the desired conditions and hexane feed introduced. Catalytic data and results are given in Table 9.

At comparable H_2 reduction times, the catalysts which were treated by heating with base solution (Catalysts C and D) showed improved yields of the isomerized 2,2-dimethylbutane product over the untreated catalysts (Catalysts A and B) at varying temperatures.

Table 6

Catalytic Data for Hexane Isomerization with Catalyst A

Temperature, °C	230	240
Pressure, psig	450	450
(kPa)	3,200	3,200
LHSV	0.6	0.6
H_2/HC	1.4/1	1.4/1
Hexane conv., wt.%	70.6	77.9
Selectivity, wt.%		
C_1-C_5	0.5	0.8
2,2-dimethylbutane	7.9	11.6
2,3-dimethylbutane	11.1	12.0
2-methylpentane	49.3	46.1
3-methylpentane	31.2	29.5
Yield, wt.%		
2,2-dimethylbutane	5.6	9.0

Table 7

Catalytic Data for Hexane Isomerization with Catalyst B

Temperature, °C	200	210	220	230
Pressure, psig	450	450	450	450
(kPa)	3200	3200	3200	3200
LHSV	0.6	0.6	0.6	0.6
H_2/HC	1.4/1	1.4/1	1.4/1	1.4/1
Hexane conv., wt.%	80.5	82.0	82.9	84.0
Selectivity, wt.%				
C_1-C_5	0.4	1.2	2.0	2.8
2,2-dimethylbutane	12.6	14.8	19.9	21.8
2,3-dimethylbutane	13.0	12.6	11.8	11.6
2-methylpentane	45.8	43.6	40.4	37.8
3-methylpentane	28.2	27.8	25.9	23.9
Yield, wt.%				
2,2-dimethylbutane	10.1	12.1	16.5	18.4

Table 8

Catalytic Data for Hexane Isomerization with Catalyst C

Temperature, °C	230	240
Pressure, psig	450	450
(kPa)	3200	3200
LHSV	0.6	0.6
H_2/HC	1.4/1	1.4/1
Hexane conv., wt.%	80.4	81.7
Selectivity, wt.%		
C_1-C_5	0.5	1.4
2,2-dimethylbutane	14.7	19.0
2,3-dimethylbutane	12.2	11.8
2-methylpentane	44.1	40.9
3-methylpentane	28.5	26.9
Yield, wt.%		
2,2-dimethylbutane	11.9	15.5

Table 9

Catalytic Data for Hexane Isomerization with Catalyst D

Temperature, °C	200	210	220	230
Pressure, psig	450	450	450	450
(kPa)	3200	3200	3200	3200
LHSV	0.6	0.6	0.6	0.6
H_2/HC	1.4/1	1.4/1	1.4/1	1.4/1
Hexane conv., wt.%	81.9	82.1	83.4	84.3
Selectivity, wt.%				
C_1-C_5	0.9	1.1	2.5	6.5
2,2-dimethylbutane	18.3	18.1	22.5	23.4
2,3-dimethylbutane	12.3	12.3	11.4	10.6
2-methylpentane	41.7	41.6	38.6	36.2
3-methylpentane	26.7	26.9	25.0	23.3
Yield, wt.%				
2,2-dimethylbutane	15.0	14.8	18.8	19.7

EXAMPLE 26

This Example describes the preparation of a further hydrothermally treated (pH ~7) zirconia support. One part by weight of the filtered wet cake from Example 16 was

mixed with 10 parts of distilled, deionized water and this mixture was refluxed with stirring for 16 hours. The mixture was cooled, filtered, and washed with 10 parts of water. The solid was air dried at 130°C for 16 hours.

EXAMPLE 27

This Example describes the preparation of a WO_x/ZrO_2 catalyst from the zirconia support described in Example 26. Approximately 5.6 parts by weight of the dried product from Example 26 was impregnated via incipient wetness with 4.2 parts of an aqueous solution containing 1 part ammonium metatungstate. The resulting material was dried in air and then calcined at 825°C in air for 3 hours.

EXAMPLE 28

This Example describes the preparation and use of a $Pt/WO_x/ZrO_2$ catalyst from the resultant product in Example 27. To 1 part of an 8% H_2PtCl_6 solution was added 2.5 parts H_2O. This mixture was then used to impregnate by incipient wetness 7 parts of the dried product (at 130°C) from Example 27. The catalyst was then calcined at 300°C in air for 2 hours. This catalyst was designated Catalyst E. In the catalytic experiments, Catalyst E was reduced with H_2 (100 cc/min) at 300°C and atmospheric pressure for 18 hours. The unit was then brought to the desired conditions and hexane feed introduced. Catalytic data and results are given in Table 10. At comparable H_2 reduction times, the catalysts which were treated by heating with aqueous solutions at pH 7-9 (Catalysts C, D, and E) showed improved yields of the isomerized 2,2-dimethyl butane product over the untreated catalysts (Catalysts A and B) at varying temperatures.

Table 10

Catalytic Data for Hexane Isomerization with Catalyst E

Temperature, °C	200	210	220
Pressure, psig	450	450	450
kPa	3200	3200	3200
LHSV	0.6	0.6	0.6
H_2/HC	1.4/1	1.4/1	1.4/1
Hexane conv., wt.%	77.8	84.0	83.7
Selectivity, wt.%			
C_1-C_5	0.4	4.3	3.7
2,2-dimethylbutane	9.9	19.7	21.4
2,3-dimethylbutane	12.8	12.4	4.0
2-methylpentane	46.6	39.4	46.2
3-methylpentane	30.3	24.2	24.7
Yield, wt.%			
2,2-dimethylbutane	7.7	16.5	18.0

Example 29

This Example describes the preparation of a hydrous zirconia support. One part by weight of zirconyl chloride, $ZrOCl_2 \cdot 8H_2O$, was dissolved in 10 parts H_2O and concentrated $NH_4OH_{(aq)}$ added until the solution pH was ~9. The resulting slurry, $Zr(OH)_4$, was filtered and washed with 10 parts of distilled, deionized water. The solid was mixed with 10 parts of distilled, deionized water, and the pH of the mixture set to pH ~9 with $NH_4OH_{(aq)}$. This mixture was refluxed for 16 hours, cooled, filtered, and washed with 10 parts of water. The solid was air dried at 130°C for 16 hours.

Example 30

This Example describes the preparation of a WO_x/ZrO_2 catalyst from the zirconia support described in Example 29. Approximately 3.3 parts by weight of the dried product from Example 29 was impregnated via incipient wetness with 2.6 parts of an aqueous solution containing 1 part of ammonium metatungstate. The resulting material was dried in air and

then calcined at 825°C in air for 3 hours. The resultant product was designated Catalyst F.

Example 31

Catalyst G was prepared analogously to Catalyst F except 1.17 parts of ammonium metatungstate was used.

Example 32

Catalyst H was prepared analogously to Catalyst F except 1.67 parts of ammonium metatungstate was used.

Examples 33-35

After calcining, Catalysts F, G and H were then impregnated with Pt via incipient wetness using a solution of 2.5 parts H_2O and 1 part 8% H_2PtCl_6. The catalysts were air dried and then calcined at 300°C in air for 2 hours.

Examples 36 and 37

Catalyst F from Example 33 was tested for hexane isomerization. In two separate runs, prior to contacting with feed hexane, the fresh catalyst was treated with H_2 (100 cc/min) at 300°C for 4 and 18 hours. Experimental conditions and catalyst results are given in Table 11.

Examples 38 and 39

Catalyst G from Example 34 was tested for hexane isomerization analogously to Examples 36 and 37. Experimental conditions and catalytic results are given in Table 12.

Examples 40 and 41

Catalyst H from Example 35 was tested for hexane isomerization. In two separate runs, prior to contacting with feed hexane, the fresh catalyst was treated with H_2 (100 cc/min) at 300°C for 4 and 72 hours. Experimental conditions and catalytic results are given in Table 13.

For Catalysts F, G, and H, increased yields of isomerized product at constant temperature were observed with the same catalysts treated with hydrogen for 18 hours instead of 4 hours. For Catalyst H, an additional experiment involving H_2 pretreatement for 72 hours was performed. Although hexane isomerization activity was

still present after the 72 hour pretreatment, the yield of 2,2-dimethylbutane was significantly lower at constant temperature than the yields obtained after 4 hours of H_2 pretreatment.

Table 11

Catalytic Data for Hexane Isomerization with Catalyst F

	4 hours		18 hours			
Temperature, °C	200	220	200	210	220	230
Pressure, psig	450	450	450	450	450	450
(kPa)	3200	3200	3200	3200	3200	3200
LHSV	0.6	0.6	0.6	0.6	0.6	0.6
H_2/HC	1.4/1	1.4/1	1.4/1	1.4/1	1.4/1	1.4/1
Hexane conv., wt.%	75.3	82.0	80.5	82.0	82.9	84.0
Selectivity, wt.%						
C_1-C_5	0.2	1.6	0.4	1.2	1.8	4.8
2,2-dimethylbutane	8.4	16.1	12.6	14.8	19.9	21.8
2,3-dimethylbutane	13.1	12.3	13.0	12.6	11.8	11.6
2-methylpentane	47.8	42.4	45.7	43.5	40.5	37.9
3-methylpentane	30.5	27.6	28.1	27.7	26.0	23.9
Yield, wt.%						
2,2-dimethylbutane	6.3	13.2	10.1	12.1	16.5	18.4

Table 12

Catalytic Data for Hexane Isomerization with Catalyst G

	4 hours			18 hours		
Temperature, °C	210	220	230	210	220	230
Pressure, psig	450	450	450	450	450	450
(kPa)	3200	320	3200	3200	3200	3200
LHSV	0.6	0.6	0.6	0.6	0.6	0.6
H_2/HC	1.4/1	1.4/1	1.4/1	1.4/1	1.4/1	1.4/1
Hexane conv., wt.%	81.6	82.7	83.6	82.1	83.4	84.3
Selectivity, wt.%						
C_1-C_5	0.4	0.9	2.5	1.1	2.5	6.5
2,2-dimethylbutane	9.5	17.4	21.6	18.1	22.5	23.4
2,3-dimethylbutane	12.5	12.2	11.3	12.3	11.4	10.6
2-methylpentane	47.4	42.2	39.3	41.6	38.6	36.2
3-methylpentane	30.2	27.3	25.4	26.9	25.0	23.3
Yield, wt.%						
2,2-dimethylbutane	6.8	14.2	17.9	14.8	18.8	19.7

Table 13

Catalytic Data for Hexane Isomerization with Catalyst H

	4 hours		72 hours	
Temperature, °C	200	220	200	220
Pressure, psig	450	450	450	450
(kPa)	3200	3200	3200	3200
LHSV	0.6	0.6	0.6	0.6
H_2/HC	1.4/1	1.4/1	1.4/1	1.4/1
Hexane conv., wt.%	79.8	84.5	48.9	76.7
Selectivity, wt.%				
C_1-C_5	0.5	3.1	0.0	0.4
2,2-dimethylbutane	14.5	25.1	2.6	10.9
2,3-dimethylbutane	21.0	11.3	11.1	12.7
2-methylpentane	36.6	37.3	52.9	46.1
3-methylpentane	27.4	23.3	33.4	29.9
Yield, wt.%				
2,2-dimethylbutane	11.6	21.3	1.3	8.44

Claims:

1. A catalyst comprising (i) an acidic solid product formed by modifying a Group IVB metal oxide with an oxyanion of a Group VIB metal and (ii) an hydrogenation/dehydrogenation component deposited on said solid product.

2. A catalyst according to claim 1 comprising a calcuated mole ratio of XO_2/YO_3, where X is said Group IVB metal and Y is said Group VIB metal, of up to 300 and from 0.001 wt% to 5 wt% of said hydrogenation/dehydrogenation component, based upon the total weight of the catalyst.

3. A catalyst according to claim 2 wherein said mole ratio is from 2 to 100 and said hydrogenation/dehydrogenation component comprises 0.001 wt% to 5 wt% of the total weight of the catalyst.

4. A catalyst according to claim 2 wherein said mole ratio is from 4 to 30 and said hydrogenation/dehydrogenation component comprises 0.1 wt% to 2 wt% of the total weight of the catalyst.

5. A catalyst according to any preceding claim, wherein said hydrogenation/dehydrogenation component comprises platinum.

6. A catalyst according to any preceding claim, wherein said hydrogenation/dehydrogenation component, in addition to said noble metal, further comprises at least one non-noble metal in the form of at least one oxide, hydroxide or metal of at least one element selected from Group VIII metals, Group IVA metals, Group VB metals and Group VIIB metals.

7. A catalyst according to claim 6, wherein said hydrogenation/dehydrogenation component further comprises tin.

8. A catalyst according to any preceding claim, wherein said Group IVB metal oxide comprises zirconia or titania.

9. A catalyst according to any preceding claim, wherein said Group VIB metal oxyanion is an oxyanion of molybdenum or tungsten.

10. A catalyst according to claim 9, wherein said source of said oxyanion of a Group VIB metal is selected from ammonium metatungstate, ammonium metamolybdate, tungsten chloride, molybdenum chloride, tungsten carbonyl, molybdenum carbonyl, tungstic acid, sodium tungstate and sodium molybdate.

11. A process for producing the catalyst of claim 1 comprising the steps of:

(a) contacting the hydroxide or hydrated oxide of a Group IVB metal with an aqueous solution comprising a source of an oxyanion of a Group VIB metal to form an acidic solid product comprising oxygen, Group IVB metal and Group VI metal; and then

(b) depositing a hydrogenation/dehydrogenation component on the solid product of step (a).

12. A process according to claim 11, wherein the solid product of step (a) is calcined at a temperature of 500 to 900°C prior to step (b).

13. A process according to claim 11, wherein the hydrated oxide of said Group IVB metal is subjected to hydrothermal treatment prior to step (a).

14. A process according to claim 13, wherein the hydrothermal treatment includes contacting the hydrated oxide with water or an aqueous hydroxide solution at a pH of at least 7 and a temperature of at least 80°C.

15. A process according to claim 11, wherein the hydroxide or hydrated oxide of the Group IVB metal is calcined at a temperature of 100 to 400°C prior to step (a).

16. A process for isomerizing C_4 to C_8 paraffin feed comprising contacting the feed with a catalyst as claimed in any one of claims 1 to 10.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/07904

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) : B01J 23/00, 23/40, 23/42, 23/44, 23/70, 23/74
US CL :Please See Extra Sheet.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 502/305, 308, 309, 310, 313, 314, 315, 316, 325, 326, 333, 334, 335, 336, 349, 350, 352

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US,A, 5,176,897 (Lester); 05 January 1993; see column 4, lines 39-69 and column 5, lines 41-69.	1-15
Y	US,A, 4,918,041 (Hollstein et al) 17 April 1990; see column 2, lines 8-36.	1-16
Y	US,A, 4,956,519 (Hollstein et al) 11 September 1990; see column 2, lines 9-37	1-16

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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Date of the actual completion of the international search	Date of mailing of the international search report
04 OCTOBER 1994	26 OCT 1994

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/07904

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A,P	US,A, 5,283,041 (Nguyen et al.) 01 February 1994, see the entire document.	1-16
Y	Arata et al., "Synthesis of Solid Superacid of Tungsten Oxide Supported on Zirconia and its Catalytic Action", Proceedings 9th International Congress on Catalysis; Volume 4, 1988, pp1727-34 see experimental and discussion, pp1728-1730.	1-16

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/07904

A. CLASSIFICATION OF SUBJECT MATTER:
US CL :

502/305, 308, 309, 310, 313, 314, 315, 316, 325, 326, 333, 334, 335, 336, 349, 350, 352